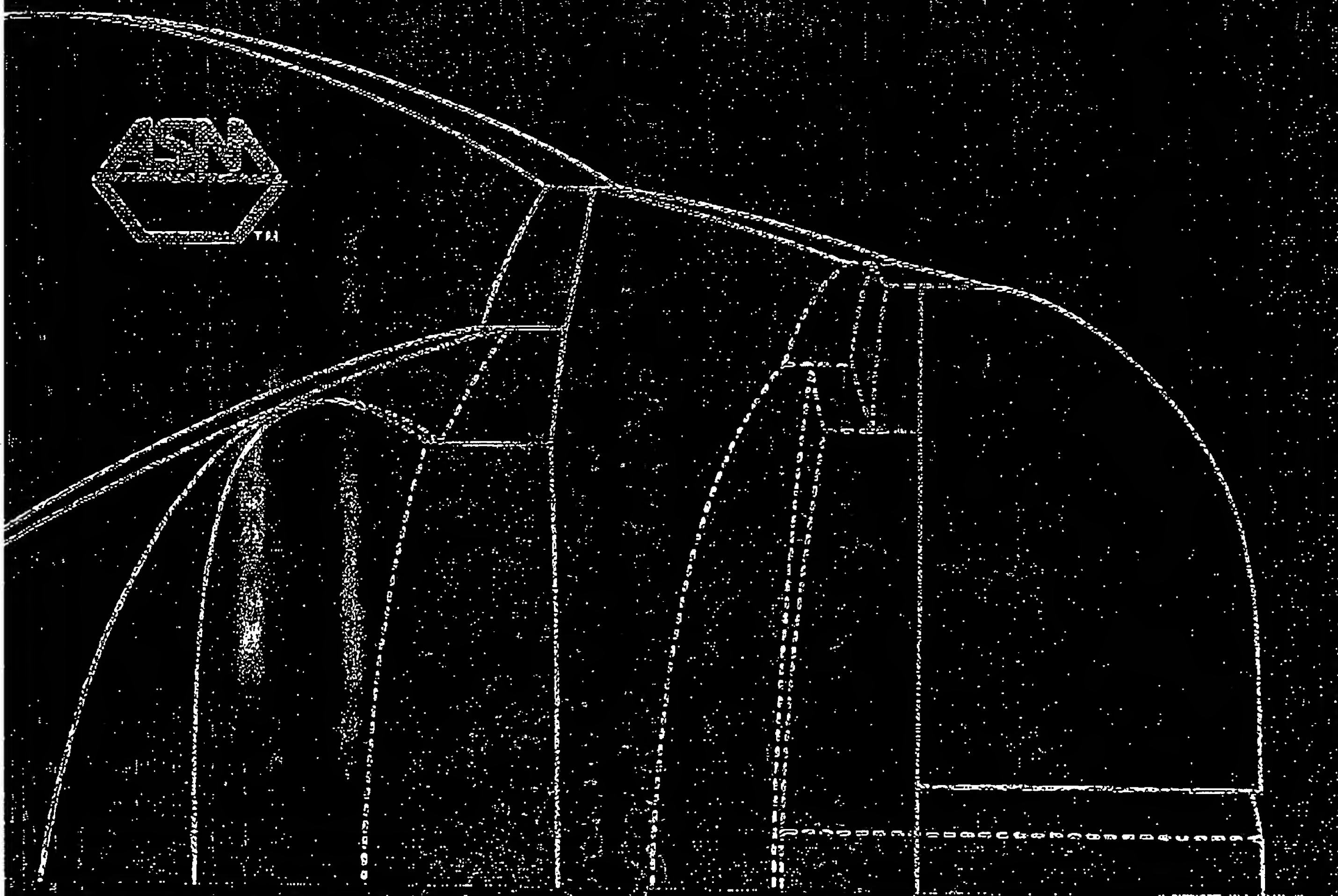
Monograph Series on Alloy Phase Diagrams

Phase Diagrams of Binary Titanium Alloys

Edited by Joanne L. Murray

ASM



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The output of the International Data Program for Alloy Phase Diagrams contained in this monograph has been reviewed by the Office of Standard Reference Data and accepted as a product of the National Standard Reference Data System.

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The Co-Ti (Cobalt-Titanium) System

58.9332 47.88

By J.L. Murray

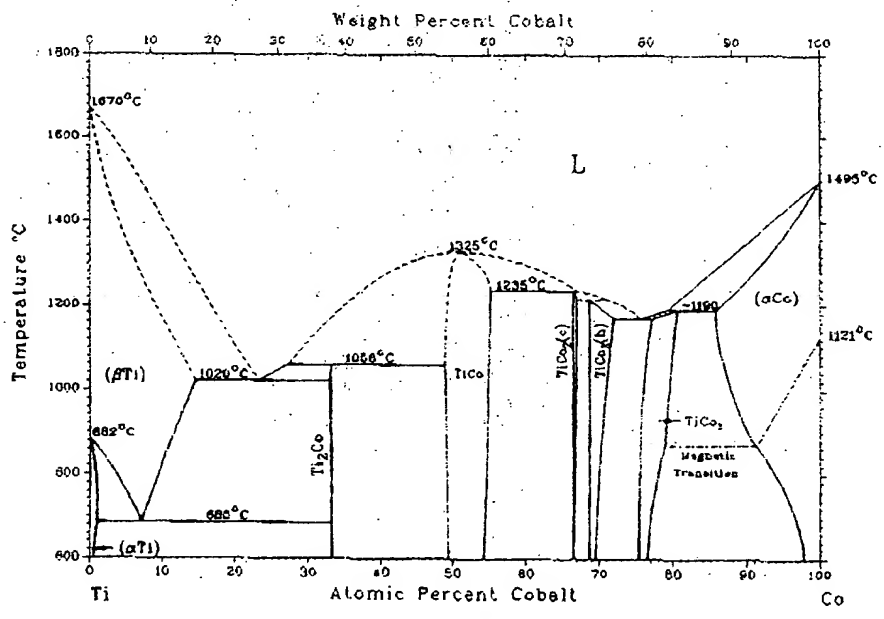
quilibrium Diagram

Certain features of the phase equilibria in the Ti-Co stem have recently been the subject of experimental ork. The phase diagram contains two "deep eutectics," in nich amorphous alloys can be formed; the higher-order rromagnetic transition has a pronounced effect on the lvus, and it is possible that the ordering transformation in supersaturated (βCo) proceeds by a spinodal mechanism. However, many important features of the diagram have received only cursory examination, or are the subject of controversy. Most notably, liquidus temperatures have not been measured in the range 0 to 20 at.% Co, and there are serious discrepancies in the range 20 to 80 at.% Co. There are conflicting reports about which of the Laves phases $TiCo_2$ are stable phases, and it has been suggested

able 1 Special Points of the Assessed Ti-Co Phase Diagram

eaction	Compositions of the respective phases, at.% Co			Temperature, °C	Reaction type
$\rightleftarrows (\beta Ti) + Ti_2Co$	23.2	14.5	32.9	1020	Eutectic
$Ti) \rightleftarrows (\alpha Ti) + Ti_2Co$	7.0	0.86	33.2	685	Eutectoid
$+ TiCo \rightleftarrows Ti_2Co$	27.1	49.0	33.1	1058	Peritectic
$\rightleftarrows TiCo$		50		1325	Congruent
$Co + L \rightleftarrows TiCo_2(c)$	55.2	67.2	66.5	1235	Peritectic
$Co_2(c) + L \rightleftarrows TiCo_3(h)$	67.0	71.0	68.75	1210	Peritectic
$\rightleftarrows TiCo_3(h) + TiCo_3$	75.8	72.0	77.2	1170	Eutectic
$+ (\alpha Co) \rightleftarrows TiCo_3$	79.3	85.9	80.7	1210	Peritectic
$\rightleftarrows (\beta Ti)$		0		1670	Melting point
$Ti) \rightleftarrows (\alpha Ti)$		0		882	Allotropic transformation
$\rightleftarrows (\alpha Co)$		100		1495	Melting point
$Co) \rightleftarrows (\varepsilon Co)$		100		421	Allotropic transformation

Fig. 1---Assessed Ti-Co Phase Diagram



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Phase Diagrams of Binary Titanium Alloys

(based on observation of polytypism) that this part of the diagram may be considerably more complex than previously assumed.

The assessed diagram is shown in Fig. 1, and special points of the diagram are listed in Table 1.

The equilibrium solid phases of the system are:

- The cph solid solutions, (αTi) and (εCo). (αTi) is stable below 882 °C, and (αCo) is stable below approximately 422 °C. The temperature range of Fig. 1 has not been extended to include the (εCo)/(αCo) transition, because the equilibrium phase relations among $TiCo_3$, (αCo), and (εCo) have not been determined experimentally.
- The bcc solid solution, (βTi), stable in pure Ti above 882 °C. The maximum solubility of Co in (βTi) is 14.5 at.% at 1020 °C.
- The fcc solid solution, (αCo), stable in pure Co above 422 °C. The maximum solubility of Ti in (αCo) is 14.1 at.% at 1190 °C.
- Ti_2Co, an ordered fcc structure containing 96 atoms per unit cell. The homogeneity range of Ti_2Co is no more than about 0.3 at.% about stoichiometry.
- TiCo, with the CsCl structure. TiCo melts congruently at 1325 °C. Its homogeneity range is 49 ± 1 to 55 ± 0.5 at.% Co at 1200 °C.
- Cubic (C15) and hexagonal (C36) Laves phases of approximate stoichiometry $TiCo_2$, here distinguished as $TiCo_2$(c) and $TiCo_2$(h), respectively. $TiCo_2$(h) is slightly richer in Co; the homogeneity ranges of $TiCo_2$(c) and $TiCo_2$(h) are approximately 66.5 to 67.0 at.% Co and 68.75 to 72 at.% Co, respectively.
- $TiCo_3$, with the ordered fcc $AuCu_3$ structure. The maximum homogeneity range of $TiCo_3$ is 75.5 to 80.1 at.% Co.

Ti-Rich Liquidus and Solidus.

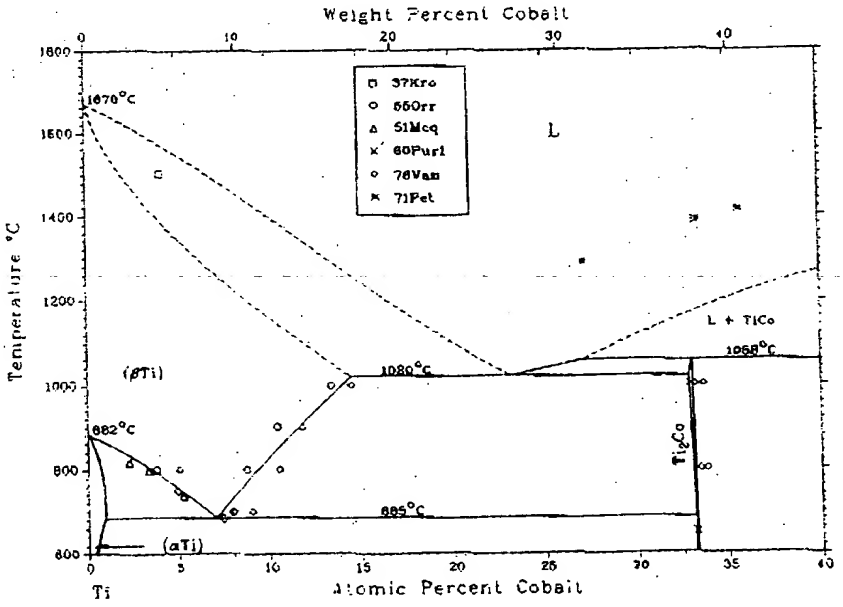
[37Kro] reported that the addition of 4.1 at.% Co lowers the melting point of Ti to approximately 1500 °C. By metallographic examination of as-cast samples, [55Orr] estimated that the solidus and liquidus curves meet the eutectic isotherm at 1020 ± 5 °C, with compositions of approximately 14.5 and 23.2 at.% Co, respectively. No other experimental work on the (βTi) solidus and liquidus has been reported. Because of the incompleteness of the experimental data on which the calculations are based, and the large temperature range over which the interpolation is made, the estimated liquidus and solidus should be viewed with considerable skepticism.

(αTi) and (βTi) Phase Equilibria.

The solubility of Co in (αTi) was estimated to be less than 0.8 at.% Co by [55Orr]. (βTi) decomposes by the eutectoid reaction (βTi) ⇌ (αTi) + Ti_2Co at 685 °C [55Orr, 63Kan]. Experimental data on the phase equilibria involving (βTi) are shown in Fig. 2.

The data of [55Orr] for the (βTi) transus are based on the original metallographic findings rather than their diagram, because their two-phase field includes several alloys that they identified as single phase. The diffusion data of [76Str] also lie to the Co-side of the other determinations. The same slight discrepancy between findings in diffusion couples and bulk alloys was noted in the Ti-Ni system. The results of diffusion experiments were therefore considered to be qualitative verification of the metallographic results, but were not used to draw the

Fig. 2---Experimental Data for the Ti-Rich Portion of the Phase Diagram



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The Ni-Ti (Nickel-Titanium) System

58.69 47.88

By J.L. Murray

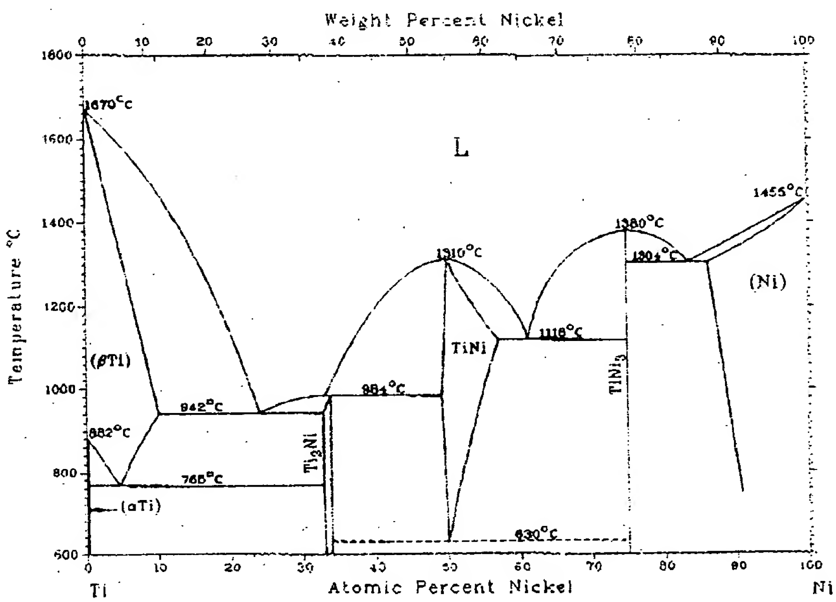
quilibrium Diagram

The Ti-Ni system is unique among Ti systems in that e liquidus and solidus are precisely determined over eir whole extent. The assessed equilibrium diagram is own in Fig. 1, and its salient points are summarized in ible 1. The system is of particular interest because of the ape memory alloys based on TiNi.

The equilibrium solid phases of the Ti-Ni system are:

- The low-temperature cph (αTi) and high-temperature bcc (βTi) solid solutions. The maximum solubility of Ni in (αTi) and (βTi) is about 0.2 and 10 at.%, respectively.
- The fcc (Ni) solid solution. The maximum solubility of Ti in (Ni) is 13.8 at.% Ti.
- Ti_2Ni, an fcc ordered structure with 96 atoms per unit cell. It is formed by a peritectic reaction at 984 °C.

Fig. 1---Assessed Ti-Ni Phase Diagram



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able 1 Special Points of the Assessed Ti-Ni Phase Diagram

eaction	Compositions of the respective phases, at.% Ni			Temperature, °C	Reaction type
⇌ (βTi) + Ti_2Ni	24	10	33.3	942	Eutectic
+ TiNi ⇌ Ti_2Ni	32	49.5	33.3	984	Peritectic
⇌ TiNi + $TiNi_3$	61	57	75	1118	Eutectic
⇌ $TiNi_3$ + (Ni)	83.5	75	86.3	1304	Eutectic
3Ti) ⇌ (αTi) + Ti_2Ni	4.5	0.2	33.3	765	Eutectoid
iNi ⇌ Ti_2Ni + $TiNi_3$	49.5	33.3	75	630	Eutectoid
⇌ TiNi		50		1310	Congruent
⇌ $TiNi_3$		75		1380	Congruent
⇌ (Ni)		100		1455	Melting point
⇌ (βTi)		0		1670	Melting point
3Ti) ⇌ (αTi)		0		882	Allotropic transformation

- TiNi, with the ordered bcc CsCl structure. TiNi melts congruently at 1310 °C and may not be an equilibrium phase below approximately 630 °C. The homogeneity range of TiNi is 49.5 to 57 at.% Ni.
- Stoichiometric $TiNi_3$, a four-layer cph ordered structure. $TiNi_3$ is formed from the liquid by a eutectic reaction at 1304 °C and melts congruently at 1390 °C.

(βTi) Liquidus and Solidus.

The Ti-rich liquidus descends to a very deep eutectic at 942 °C, with a eutectic composition of 24 at.% Ni. The maximum solubility of Ni in (βTi) is 10 at.% at 942 °C. In addition to the eutectic temperature and composition, accurate data are available for the whole extent of the liquidus and solidus [54Poo]. The (βTi) liquidus measurements were part of a complete determination of the diagram above 850 °C by [54Poo]. The liquidus was measured by a microscopic technique developed for treating reactive, high-melting metals [54Hum]. Microscopic and X-ray methods were used to determine the solidus. Experimental data are shown in Fig. 2; experimental determinations of the invariant temperatures are summarized in Table 2. The determinations by [49Lon] and [53Mar] agree qualitatively with [54Poo], but because they are less accurate, only the data of [54Poo] are used to determine the assessed phase boundaries.

(αTi)/(βTi) Boundaries and Eutectoid Reaction.

[53Mar] estimated the solubility of Ni in (αTi) to be less than 0.2 at.%, based on microscopic examination of equilibrated alloys, and this is the only information presently available on the (αTi) solvus. In the following discussion, the (βTi)/(βTi) + (αTi) and the (βTi)/(βTi) + Ti_2Ni boundaries are designated the (βTi) transus and (βTi) solvus respectively. The (βTi) transus and solvus intersect at a eutectoid point at 4.5 at.% Ni and 765 °C.

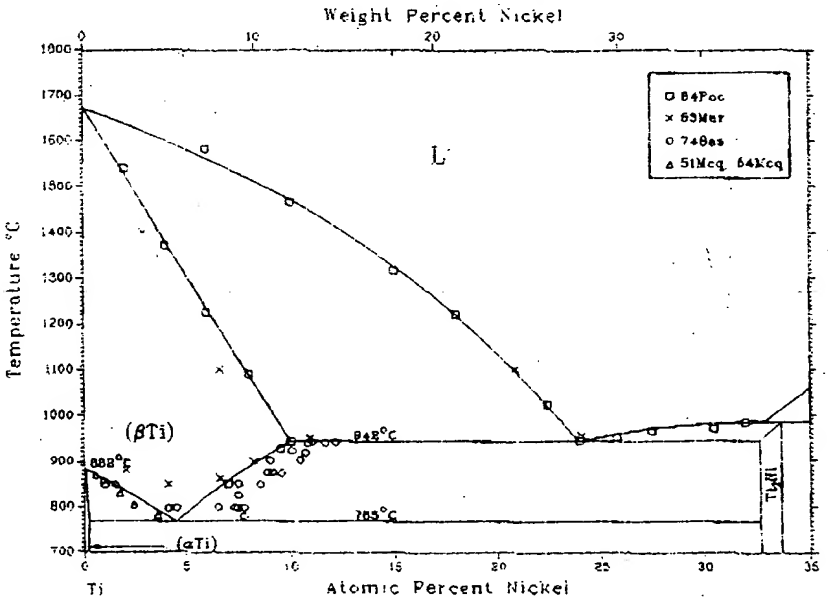
The (βTi) phase equilibria were examined by [53Mar], [54Mcq], and [54Poo] using metallography. [51Mcq] used the hydrogen pressure technique, and [74Bas] used microprobe analysis of equilibrated two-phase alloys and annealed diffusion couples. [51Mcq] and [54Mcq] examined the (βTi) transus only, [54Poo] the solvus only, and [53Mar] and [74Bas] both boundaries. The discrepancies are striking. Figure 2 includes a detail of the eutectoid region.

For a given composition, the (βTi) transus of [51Mcq] lies at the lowest temperature, and that of [53Mar] lies at the highest temperature, with [74Bas] in between. The [53Mar] results can be discounted as inconsistent with the thermodynamic properties of pure Ti. [54Mcq] attributed the discrepancy to the decomposition of single-phase (βTi) during an insufficiently rapid quench, and this explanation can be accepted as consistent with observations on many Ti-based eutectoid systems and with studies of the (βTi)/(αTi) martensite transformation. Hydrogen pressure results, however, consistently lie below the best metallographic work for several Ti systems. The (βTi) transus data of [74Bas] come from diffusion couple experiments only, and it cannot be accurately judged how closely these experiments represent equilibrium. For the (βTi) solvus, [74Bas] also examined equilibrated bulk alloys. The EPMA determinations lie in a band about 2 at.% wide about 1 at.% to the Ni-rich side of the metallographic work [53Mar, 54Poo].

The assessed solvus is based primarily on the work of [54Poo]; the assessed (βTi) transus lies above that of [51Mcq] and [54Mcq], but slightly below that of [74Bas].

Assessment of this part of the diagram is hampered by the absence of a reliable direct determination of the

Fig. 2---Experimental Data on the Ti-Rich Portion of the Ti-Ni Phase Diagram



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